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(54) SOLUTION EXTRUSION OF POLYPHENYLENE ETHER
COMPOSITIONS

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The invention relates to a novel process for preparing thermoplastic compositions of a polyphenylene ether resin and a vinyl aromatic resin which employs solution extrusion.

5 The term "polyphenylene ether resin" includes a family of polymers well known to those skilled in the art, and they are made by a variety of catalytic and non-catalytic processes from the corresponding phenols or reactive derivatives thereof. By way of illustration, 10 certain of the polyphenylene ethers are disclosed in Hay U.S. Patent 3,306,874 dated February 28, 1967 and 3,306,875 dated February 28, 1967, and in Stamatoff, U.S. patent No. 3,257,357 dated June 21, 1966 and Patent # 3,257,358 dated June 21, 1966. In the Hay patents, 15 the polyphenylene ethers are prepared by an oxidative coupling reaction comprising passing an oxygen-containing gas through a reaction solution of a phenol and a metal -

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amine complex catalyst. Other disclosures relating to processes for preparing polyphenylene ether resins, including graft copolymers of polyphenylene ethers with styrene type compounds, are found in Fox, U.S. 3,356,761; Sumitomo, U.K. 1,291,609; Bussink et al, U.S. 3,337,499; Blanchard et al, U.S. 3,219,626; Laakso et al, U.S. 3,342,892; Borman, U.S. 3,344,166; Hori et al, U.S. 3,384,619; Faurote et al, U.S. 3,440,217; and disclosures relating to metal based catalysts which do not include amines, are known from patents such as Wieden et al, U.S. 3,442,885 (copper-amidines); Nakashio et al, U.S. 3,573,257 (metal-alcoholate or -phenolate); Kobayashi et al, U.S. 3,455,880 (cobalt chelates); and the like. In the Stamatoff patents, the polyphenylene ethers are produced by reacting the corresponding phenolate ion with an initiator, such as peroxy acid salt, an acid peroxide, a hypohalite, and the like, in the presence of a complexing agent. Disclosures relating to non-catalytic processes, such as oxidation with lead dioxide, silver oxide, etc., are described in Price et al, U.S. 3,382,212. Cizek, U.S. 3,383,435 discloses polyphenylene ether-styrene resin compositions.

The Cizek patent discloses a method of preparing styrene resin compositions by dry blending the compositions and then melt blending the dry blend in an extruder. This process requires the preparation of the polyphenylene ether in dry form

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free of the solvent system in which it was formed by the oxidative coupling of a phenolic monomer. Applicant has discovered that if the phenolic monomer is polymerized in a suitable solvent system, a vinyl aromatic compound may be dissolved in the reaction solution and that composition may be solvent extruded to form a dry extrudate in a single step process. This is highly advantageous as it eliminates the need for a separate system for the precipitation and drying of the polyphenylene ether resin.

10 Accordingly, it is a principal object of this invention to provide an improved method of preparing a polyphenylene ether resin-vinyl aromatic resin composition.

It is also an object of this invention to provide a method for preparing a polyphenylene ether resin-vinyl aromatic resin composition which eliminates the need to separate the polyphenylene ether resin from the solvent in which it is prepared.

U.S. 3,437,638 to Bottenbruck et al discloses a method for the separation of solvent from a polycarbonate solution which is based on the extrusion of a mixed solvent solution of polycarbonate. The polycarbonate solvent extrusion process was employed only to reduce residual chlorine by means of the added second solvent. No compositions are directly formed in the Bottenbruck et al process.

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Description of the Invention - According to the present invention, there is provided a method of producing a composition of a polyphenylene ether resin and a vinyl aromatic resin, said method comprising providing a solution of said polyphenylene ether in a high boiling solvent, and thereafter, extruding the solution through a devolatilizing extruder to remove said high boiling solvent to form a substantially solvent free composition.

10 The extrusion step is carried out in a devolatilizing extruder that is provided with a vacuum venting means which facilitates solvent removal during high speed extrusion.

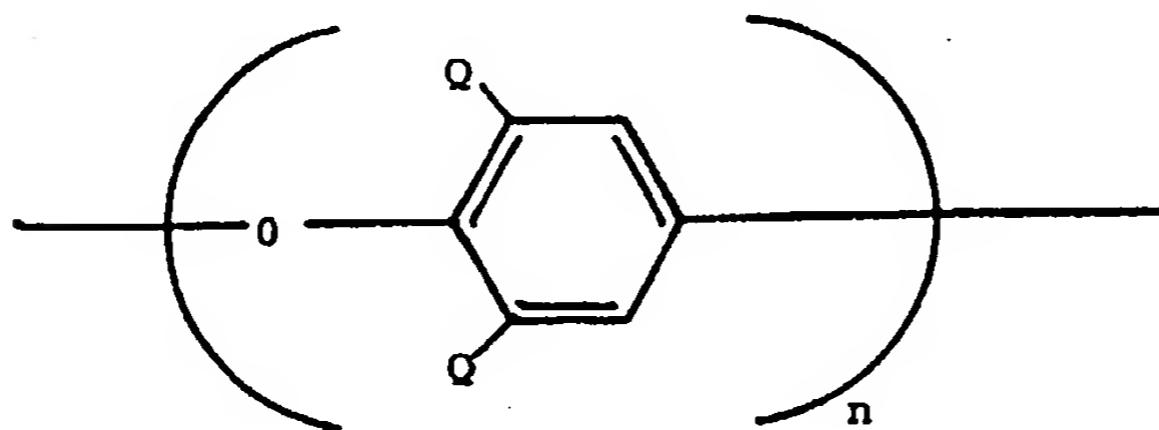
Prior to extrusion, it is preferred to concentrate the polymer solution by removing a portion of the solvent. The solvent should be capable of dissolving the polyphenylene ether resin and the vinyl aromatic resin. Suitable high boiling solvents may be found in the above referenced Hay patents. The preferred solvents are chlorobenzene and toluene.

20 The preferred extruder for this process is a devolatilizing, self-cleaning, twin-screw extruder such as the one made by Werner & Pfleiderer Co. of Stuttgart, Germany. Preconcentration of the polymer can be effected in an APV type evaporator or a wiped film evaporator. The main requirement is good heat transfer and low skin (surface) temperature to minimize polymer degradation and equipment fouling.

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Extrusion temperatures of from 190-330°C may be employed depending on the solvent and the rate of extrusion. If vacuum venting is employed, reduced pressures of 10-100 mm of Hg. may be employed.

The polyphenylene ether resins are preferably of the type having the repeating structural formula:

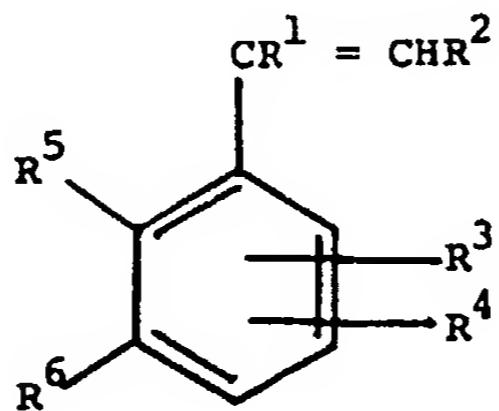


wherein the oxygen ether atom of one unit is connected to the benzene nucleus of the next adjoining unit, n is a positive integer and is at least 50, and each Q is a monovalent substituent selected from the group consisting of hydrogen, halogen, hydrocarbon radicals free of a tertiary alpha carbon atom, halohydrocarbon radicals having at least two carbon atoms between the halogen atom and the phenyl nucleus, hydrocarboxy

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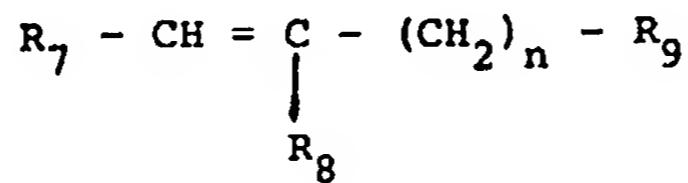
radicals and halohydrocarboxy radicals having at least two carbon atoms.

The vinyl aromatic resins are preferably of the type wherein at least 25% of the units of said vinyl aromatic resin are of the formula:



wherein R¹ and R² are selected from the group consisting of lower alkyl or alkenyl groups of from 1 to 6 carbon atoms and hydrogen; R³ and R⁴ are selected from the group consisting of chloro, bromo, hydrogen and lower alkyl of from 1 to 6 carbon atoms; R⁵ and R⁶ are selected from the group consisting of hydrogen and lower alkyl and alkenyl groups of from 1 to 6 carbons or R⁵ and R⁶ may be concatenated together with hydrocarbyl groups to form a naphthyl group.

Materials that may be copolymerized with the units of the vinyl aromatic monomer include those having the general formula:



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wherein R_8 and k_7 represent a substituent selected from the group consisting of hydrogen, halogen, an alkyl group of 1-4 carbon atoms, carboalkoxy or R_7 and R_8 taken together represent an anhydride linkage ($-COOC-$) and R_9 is hydrogen, vinyl and alkyl or alkenyl group having 1-12 carbon atoms, cycloalkyl having 3 to 6 carbon atoms, carboalkoxy having 2 to 6 carbon atoms, alkoxy-alkyl having 2 to 6 carbon atoms, alkylcarboxy having 2 to 6 carbon atoms, ketoxy halogen, carboxy having 1 to 6 carbon atoms, cyano, pyridyl and n is a whole number between 0 and 9.

10

The general formulas set forth above include by way of example, homopolymers such as homopolystyrene and monochloro-polystyrene, the modified polystyrenes, such as rubber-modified, high-impact polystyrene and the styrene containing copolymers, such as the styrene acrylonitrile copolymers, styrene butadiene copolymers, styrene-acrylonitrile-2-alkyl styrene copolymers, poly-2-methylstyrene, copolymers of ethylvinylbenzene and divinylbenzene and styrene maleic anhydride copolymers.

20

The styrene-maleic anhydride copolymers are described in U.S. 2,971,939; U.S. 3,336,267 and U.S. 2,769,804.

The rubber-modified, high- impact styrene resins are preferred and these may be made by well known procedures with rubbers such as nitrile rubbers, polybutadiene rubber, styrene-

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butadiene rubber, polysulfide rubber, ethylene-propylene copolymers and EPDM rubbers.

The compositions prepared by the process of this invention may comprise from 99-1 parts by weight of a polyphenylene ether resin and from 1-99 parts by weight of a vinyl aromatic resin.

Other additives such as fillers, processing aids, reinforcing fillers, flame retardants and the like may be employed in the compositions prepared by the method of this invention.

10 Reinforcing fillers such as 1-80% by weight of filamentous glass may be added to the solution prior to extrusion. Agitation may be used to maintain a homogenous dispersion prior to extrusion. Flame retardants such as those mentioned in U.S. 3,671,487 dated June 20, 1972 may also be added prior to extrusion.

Description of the Preferred Embodiment -

EXAMPLE

20 A solution of 25% w/w of poly(2,6-dimethyl-1,4-phenylene) ether in chlorobenzene is obtained in accordance with the teachings of Hay, U.S. 3,306,876. The catalyst is removed by extraction and the temperature of the solution is raised to

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150°F. This is combined with an amount of rubber-modified, high-impact polystyrene (Foster Grant 834) that is equal to the amount of poly(2,6-dimethyl-1,4-phenylene) ether. This forms a solution of the two materials with some of the rubber-modified, high-impact polystyrene slurried in. The solution is fed to a devolatilizing extruder (ZDS K-28 Werner Pfleiderer) where the solvent is removed and a dry extrudate is obtained which is chopped into molding pellets. The devolatilizing extruder is operated at a temperature of 190°-310° and under a vacuum venting of 25 mm Hg.

10

By the term "high boiling" solvent as used herein is meant solvents which boil over about 100°C and have a vapor pressure sufficiently high enough to permit them to be readily stripped off at a temperature which does not cause decomposition of the polymeric materials.

Useful solvents include toluene, xylene, nitrobenzene, o-dichlorobenzene, tetrachloroethylene, dichlorobenzene, t-amylalcohol and the like.

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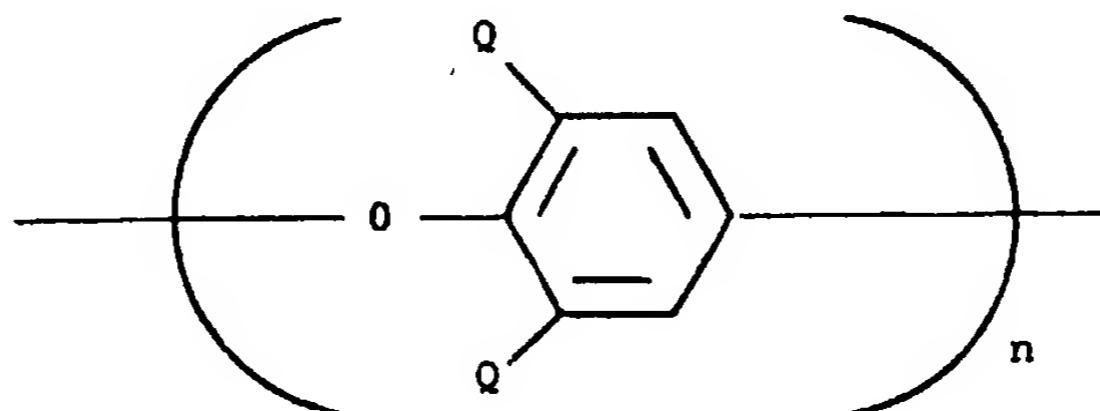
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Obviously other modifications and variations of the present invention are possible in the light of the above teachings. It is, therefore, to be understood that changes may be made in the particular embodiments of the invention described which are within the full intended scope of the invention as defined by the appended claims.

5

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A method of producing a composition of a polyphenylene ether resin and a vinyl aromatic resin, said method comprising providing a solution of said polyphenylene ether and said vinyl aromatic resin in a high boiling solvent, and thereafter, extruding the solution through a devolatilizing extruder to remove said high boiling solvent to form a substantially solvent-free composition.
2. The method of claim 1 wherein the solution of said polyphenylene ether and said vinyl aromatic resin is concentrated prior to extrusion.
3. The method of claim 1 wherein said polyphenylene ether resin is of the formula:

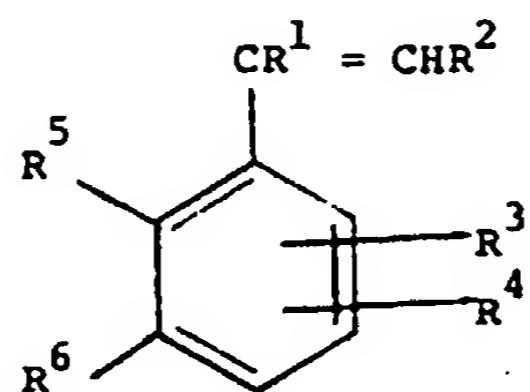


wherein the oxygen ether atom of one unit is connected to the benzene nucleus of the next adjoining unit, n is a positive integer and is at least 50, and each Q is a monovalent substituent selected from the group consisting of hydrogen, halogen,

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hydrocarbon radicals free of a tertiary alpha carbon, halo-hydrocarbon radicals having at least two carbon atoms between the halogen atom and the phenyl nucleus, hydrocarbonoxy radicals having at least two carbon atoms.

4. The method of claim 1 wherein said vinyl aromatic resin has at least 25% of its units derived from a monomer of the formula:



wherein R^1 and R^2 are selected from the group consisting of lower alkyl or alkenyl groups of from 1 to 6 carbon atoms and hydrogen; R^3 and R^4 are selected from the group consisting of chloro, bromo, hydrogen and lower alkyl of from 1 to 6 carbon atoms; R^5 and R^6 are selected from the group consisting of hydrogen and lower alkyl and alkenyl groups of from 1 to 6 carbon atoms or R^5 and R^6 may be concatenated together with hydrocarbyl groups to form a naphthyl group.

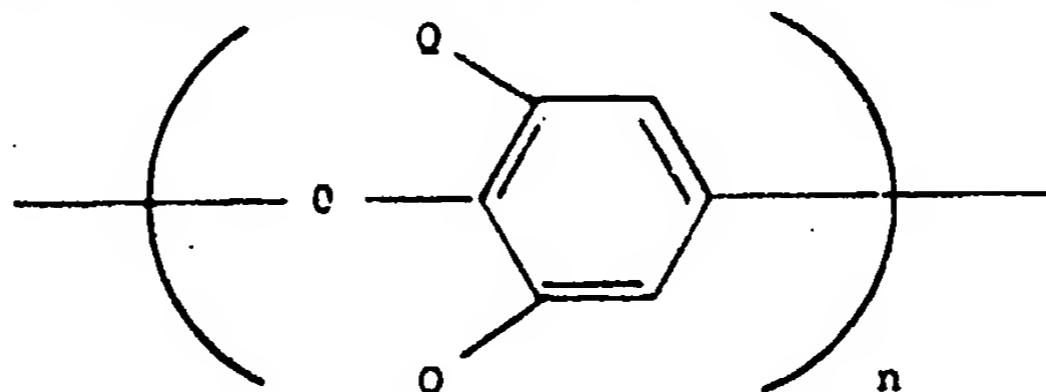
5. The method of claim 1 wherein said composition includes a reinforcing amount of a reinforcing filler.

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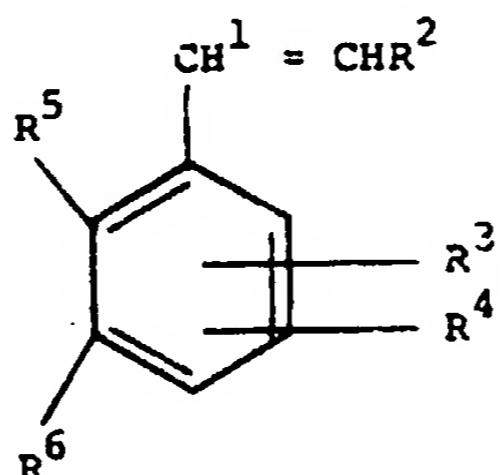
6. The method of claim 1 wherein said composition includes a flame retardant agent.

7. The method of claim 5 wherein said composition includes a flame retardant agent.

8. A method of producing a composition of from 99-1 parts by weight of a polyphenylene ether resin of the formula:



wherein the oxygen ether of one unit is connected to the benzene nucleus of the next adjoining unit, n is a positive integer and is at least 50, and each Q is a monovalent substituent selected from the group consisting of hydrogen, halogen, hydrocarbon radicals free of a tertiary alpha carbon atom, halo hydrocarbon radicals having at least two carbon atoms between the halogen atom and the phenyl nucleus, hydrocarboxy radicals having at least two carbon atoms and from 1-99 parts by weight of a vinyl aromatic resin that has at least 25% of its units derived from a monomer of the formula:



wherein R¹ and R² are selected from the group consisting of lower alkyl or alkenyl groups of from 1 to 6 carbon atoms and hydrogen; R³ and R⁴ are selected from the group consisting of chloro, bromo, hydrogen and lower alkyl of from 1 to 5 carbon atoms; R⁵ and R⁶ are selected from the group consisting of hydrogen and lower alkyl and alkenyl groups of from 1 to 6 carbon atoms or R⁵ and R⁶ may be concatenated together with

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hydrocarbyl groups to form a naphthyl group said method comprising providing a solution of said polyphenylene ether and said vinyl aromatic resin in a high boiling solvent and thereafter extruding the solution through a devolatilizing extruder at a temperature of 190-330°C at a reduced pressure of 10-100 mm of Hg. to remove said high boiling solvent and form a substantially solvent-free composition.

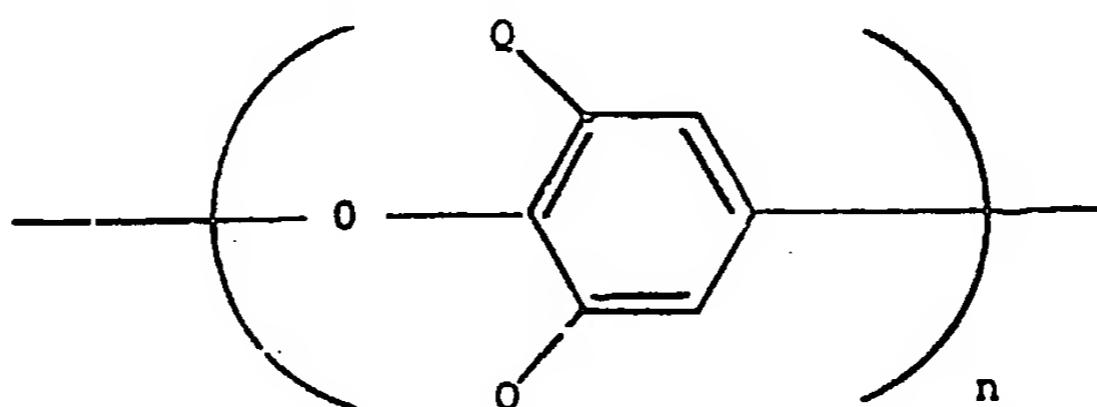
9. A method as defined in claim 8 wherein 1-80% of glass fibers are added to the solution prior to extrusion.

10. A method as defined in claim 5 wherein 1-80% of glass fibers is added prior to extrusion.

11. A method as defined in claim 8 wherein the polyphenylene ether resin is poly(2,6-dimethyl-1,4-phenylene ether).

12. A method as defined in claim 9 wherein the polyphenylene ether resin is poly(2,6-dimethyl-1,4-phenylene ether).

13. A method of producing a composition of from 99-1 parts by weight of a polyphenylene ether resin of the formula:



wherein the oxygen ether of one unit is connected to the benzene nucleus of the next adjoining unit, n is a positive integer and is at least 50, and each Q is a monovalent substituent selected from the group consisting of hydrogen, halogen, hydrocarbon radicals free of a tertiary alpha carbon atom, halo-hydrocarbon radicals having at least two carbon atoms between the halogen atom and the phenyl nucleus, hydrocarbonoxy radicals

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Claim 13 continued:

having at least two carbon atoms and from 1-99 parts by weight of a styrene resin, said method comprising providing a solution of said polyphenylene ether resin and said styrene resin in a solvent selected from the group consisting of chlorobenzene and toluene and thereafter extruding the solution through a devolatilizing extruder at a temperature of 190-330°C at a reduced pressure of 10-100 mm of Hg. to remove said solvent and form a substantially solvent-free composition.

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